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**COMPUTER MODELING OF SOOT FORMATION  
COMPARING FREE RADICAL AND IONIC MECHANISMS**

(A Collaborative Project between AeroChem and Penn State)

**Annual Technical Report**  
of the Penn State Efforts (Grant No. AFOSR 88-0072)

Covering the period from December 1, 1988 to November 30, 1989

prepared for  
**AIR FORCE OFFICE OF SCIENTIFIC RESEARCH**  
Bolling AFB

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## INTRODUCTION

This is a second annual report on collaborative study between AeroChem Research Laboratories (principal investigator – Dr. H. F. Calcote) and the Pennsylvania State University (principal investigator – Dr. M. Frenklach). The ultimate objective of this program is to develop a quantitative physical/chemical model of the mechanism of soot formation that is consistent with available experimental data. The specific objectives of the proposed 3-year study are: 1) to delineate the relative importance of radical and ionic mechanisms of soot nucleation in flames, and 2) to determine the optimum chemical and physical model of the total soot formation process. Only the Penn State work is reported here, that of AeroChem IS reported in their annual report.<sup>1</sup>

## WORK PROPOSED

The specific objectives proposed for the second year of the of the Penn State efforts were:

1. To undertake and complete the analysis of the flame simulations with the ion-reaction mechanism provided to us by AeroChem.
2. To complete the overall analysis of the competition of the PAH formation between the ionic and radical mechanisms.
3. To review the reactions and the associated rate and thermochemical data for the production of larger species and soot particles developed by AeroChem.
4. To develop a computer code for modeling the formation and growth of large-sized species and soot particles.
5. To perform computer simulation of soot particle formation in flames with the code developed.

## RESULTS

During the last twelve-months period of the project, we completed most of the planned work: the ion reaction mechanism provided to us by AeroChem was "cleaned-up" and run with a flame code, the computational results were analyzed, a computer code for modeling large species and soot particle formation and growth was developed, our neutral reaction mechanism was updated and tested, and a detailed computer simulation of soot particle nucleation and growth in laminar premixed flames was successfully performed using our updated neutral reaction mechanism. The latter part is a particularly significant accomplishment, as it is for the first time soot particle

inception could be modeled from first principles, starting with fuel decomposition and going all a way to predicting, in quantitative agreement with experiment, soot particle properties.

### Ion Reaction Mechanism

The flame simulation using the mechanism provided to us by AeroChem<sup>2</sup> was completed. The initial results indicated that a number of the rate coefficients are greatly overestimated at low temperatures, causing severe numerical problems with the flame simulations. This problem was corrected by estimating the rate coefficients for the exothermic direction and by calculating the rate coefficients for the reverse, endothermic direction from the principal of detailed balancing, as was advocated in our work on the neutral reaction mechanism.<sup>3</sup> The results computed with this corrected mechanism were essentially the same as those obtained in the preliminary runs:<sup>4</sup> the formation of polycyclic aromatic hydrocarbons (modeled in our work up to the size of coronene, C<sub>24</sub>H<sub>12</sub>) via the ionic reaction pathway is much slower than that via the pathway involving neutrals. The factors responsible for that are:<sup>4</sup> (1) a relatively low rate of chemi-ionization as compared to that of radical production at the same conditions, and (2) reversibility of the reaction steps responsible for the formation of high-molecular weight species. The latter condition is what make the reaction network so complex, to the extent that no simple analysis based on equilibrium assumptions or irreversible kinetics can be applied.

We also performed flame simulations with a newer ion reaction mechanism of AeroChem. The results, as far as the ions-vs-neutrals competition is concerned, were again the same as those obtained with the previous mechanisms, and discussed above. These results, however, cannot be taken as final, because the ion reaction mechanism is not yet completely updated and tested.<sup>1</sup> For example, in the present state, it produces an order of magnitude higher total concentration of ions than determined in experiment.<sup>5</sup> This point and others will have to be resolved in the future work.

### Neutral Reaction Mechanism

Accurate prediction of polycyclic aromatic hydrocarbons (PAHs) in flames is critical for modeling of soot formation in hydrocarbon combustion. In our initial efforts, the objective was a proof-of-a-concept computer simulation of PAH production in high-temperature hydrocarbon pyrolysis,<sup>3</sup> and later, in a low-pressure laminar premixed acetylene flame.<sup>6</sup> Now, when the acetylene-addition mechanism we have advocated for the last five years is well tested under various experimental conditions and by different research groups, the objective is to improve the mechanism to a point that it is capable of *quantitative* predictions. Preliminary results of such efforts are reported below.

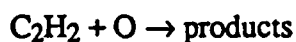
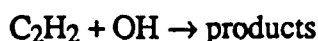
We chose to model the PAH profiles in three well-studied laminar premixed flames, whose conditions are summarized in the following table:

Table 1. Flame conditions

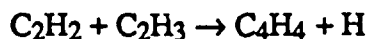
No.	Composition in Argon	P (torr)	Cold gas velocity (cm/s)	Reference
1	46.5% C <sub>2</sub> H <sub>2</sub> – 48.5% O <sub>2</sub>	20	50	MIT group <sup>7</sup>
2	23.6% C <sub>2</sub> H <sub>2</sub> – 21.4% O <sub>2</sub>	90	20	Bockhorn <i>et al.</i> <sup>8</sup>
3	16.5% C <sub>2</sub> H <sub>4</sub> – 17.9% O <sub>2</sub>	760	7.8	Harris <i>et al.</i> <sup>9</sup>

These flames were computed using the Sandia burner code.<sup>10</sup> The Lennard-Jones parameters of PAH molecules were calculated using empirical correlations and available physical properties.<sup>11</sup> The transport coefficients obtained in this manner agreed well with experimental data available for several compounds. The thermodynamic data were taken from Stein and Fahr,<sup>12</sup> except for the C–H group additivity which was based on the recent results of Green *et al.*<sup>13</sup>

The reaction mechanism is composed of two parts: the small molecule reactions, responsible for the main flame structures; and reactions describing the formation and growth of PAHs. The reaction mechanism for the former part was composed of data taken primarily from several sources: (a) our recently optimized methane oxidation mechanism,<sup>14</sup> (b) revised mechanism of Frenklach and Warnatz,<sup>6</sup> and (c) revised acetylene oxidation mechanism of Hwang *et al.*<sup>15</sup> The main revisions included: the rate coefficients of acetylene–hydroxyl, and acetylene–oxygen atom reactions

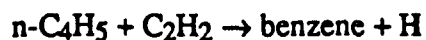


were taken from Miller and Melius,<sup>16</sup> and Mahmud and Fontijn,<sup>17</sup> respectively. The rate coefficient for reaction



was taken from Fahr and Stein.<sup>18</sup>

The formation of the first aromatic ring followed the basic reaction scheme of Frenklach and Warnatz,<sup>6</sup>



however with the rate coefficients taken from the work of Westmoreland *et al.*,<sup>19</sup> who used a QRRK methodology of estimating chemical activation processes involved in these reactions. The assignment of the rate coefficients for the main reaction classes responsible for PAH growth are summarized in Table 2.

Table 2. Revision of rate coefficients for main reaction classes of PAH growth

Reaction	Prototype reaction	Reference
$\text{aryl-H} + \text{H} \rightarrow \text{aryl} + \text{H}_2$	$\text{benzene} + \text{H} \rightarrow \text{phenyl} + \text{H}_2$	Kiefer <i>et al.</i> <sup>20</sup>
$\text{aryl} + \text{C}_2\text{H}_2 \rightarrow \text{aryl-C}_2\text{H} + \text{H}$	$\text{phenyl} + \text{C}_2\text{H}_2 \rightarrow \text{phenyl-acetylene} + \text{H}$	Fahr and Stein <sup>18</sup>
$\text{aryl} + \text{O}_2 \rightarrow \text{products}$	$\text{phenyl} + \text{O}_2 \rightarrow \text{products}$	Lin and Lin <sup>21</sup>

The computational results for the three flames are presented in Figures 1 to 6. These results were obtained with the rate coefficients for several small-molecule reactions adjusted by a factor of 2 to 3, still within their experimental uncertainties. As can be seen in these figures, the agreement between the modeling predictions and experimental data is good for major species. The agreement for PAHs is not exactly quantitative, but certainly much closer — in both shape and absolute values — than reported previously.<sup>6</sup> The important result here is that the near-quantitative accuracy was obtained for PAHs with a single reaction mechanism for all the three flames simultaneously. The major reaction pathways, their roles in PAH growth, and the sensitivity information are essentially the same as reported and discussed in the previous work.<sup>6</sup>

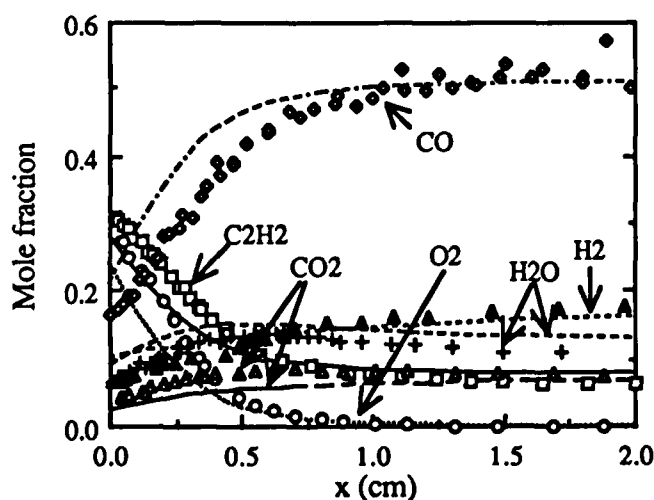


Figure 1. Computed vs. experimental major species concentrations of Flame 1.

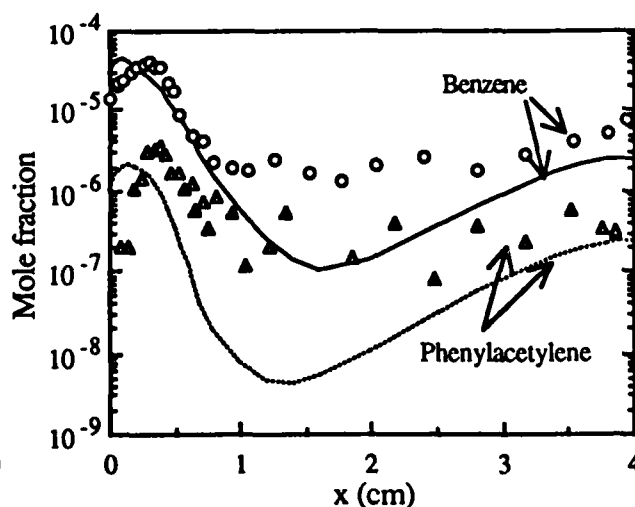


Figure 2. Computed vs. experimental major aromatic species concentrations of Flame 1.

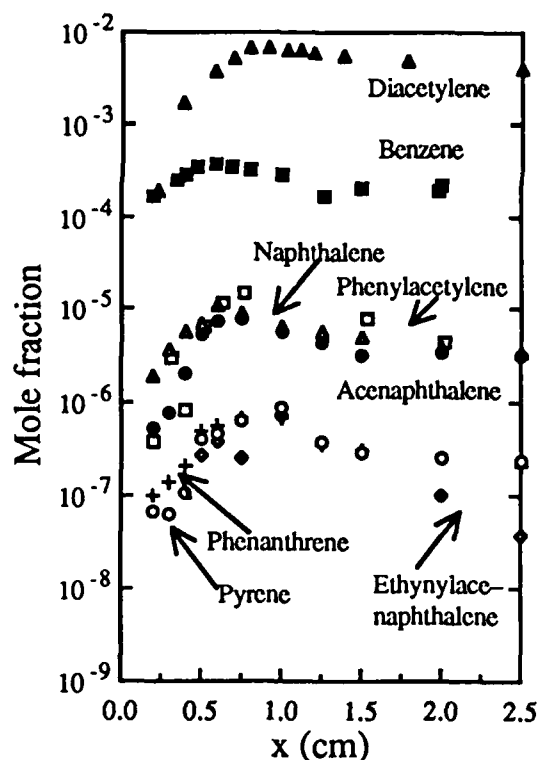


Figure 3. Measured mole fractions of diacetylene and selected PAHs of Flame 2.

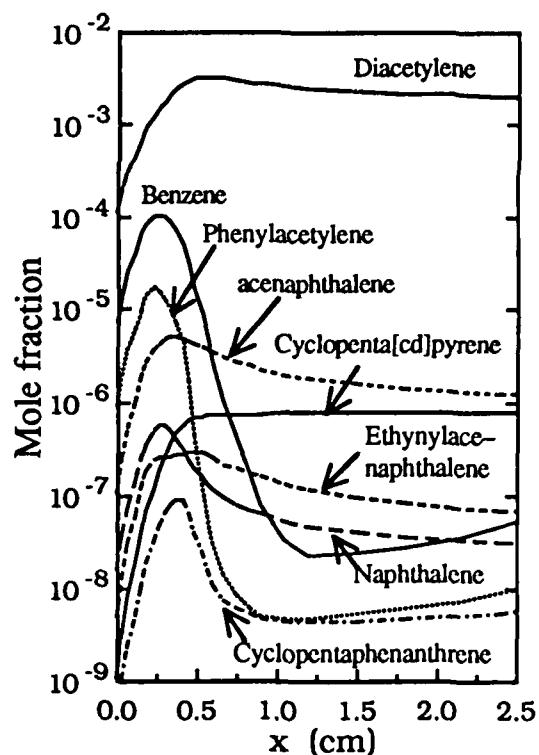


Figure 4. Computed mole fractions of diacetylene and PAHs of Flame 2.

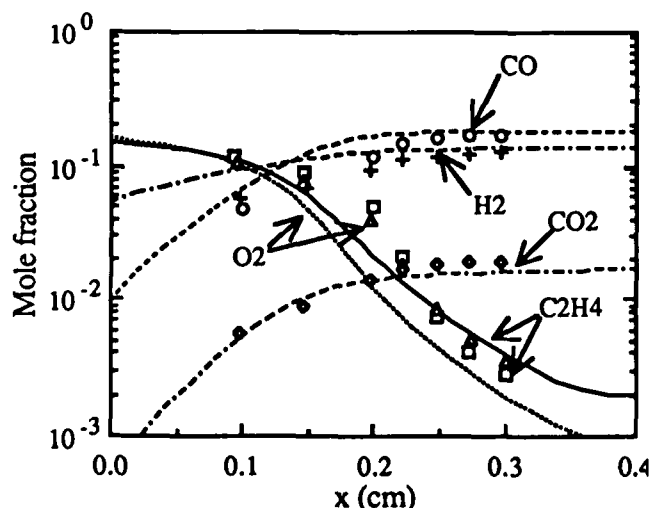


Figure 5. Computed vs. experimental major species concentrations of Flame 3.

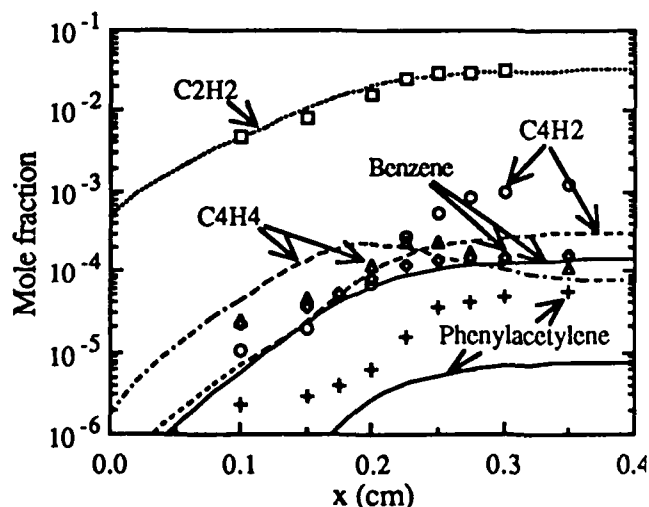


Figure 6. Computed vs. experimental minor species concentration of Flame 3.

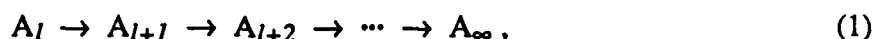
Further work on improving the prediction of PAH profiles under the flame conditions and analysis of the factors affecting it is in progress.



## Flame Simulation of Soot Particle Nucleation and Growth

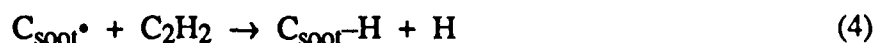
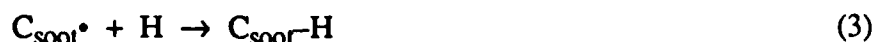
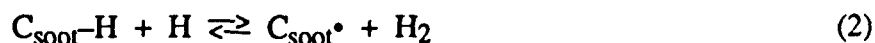
Using the neutral reaction mechanism described in the previous section, we performed detailed modeling of soot particle nucleation and growth in several laminar premixed flames. The computational model consists of three logical parts: (I) *initial PAH formation*, which includes a detailed chemical kinetic description of acetylene pyrolysis and oxidation, formation of the first aromatic ring, and its subsequent growth to a prescribed size; (II) *planar PAH growth*, comprised of replicating-type growth of PAHs beyond the prescribed size; and (III) *spherical particle formation and growth*, consisting of coagulation of PAHs formed in part (II) followed by the growth of the resulting particles by coagulation and surface reactions.

The initial part of the particle dynamics model, *nucleation*, describes the planar growth of PAHs via the H-abstraction/C<sub>2</sub>H<sub>2</sub>-addition reaction sequence<sup>3,6</sup> using the technique of chemical lumping.<sup>22,23</sup> This method provides a mathematically rigorous description of the growth process to an infinite size PAH, which can be schematically represented as



where  $A_l$  represents an aromatic species containing  $l$  fused rings. The PAH species formed in (1) are then allowed to *coagulate*, that is, all the  $A_i$ 's ( $i = l, l+1, \dots, \infty$ ) collide with each other forming dimers; the dimers, in turn, collide with  $A_i$  forming trimers or with other dimers forming tetramers; and so on. The coalescence reactions were treated as irreversible having sticking coefficients of unity. As the focus of this work was on very young, small particles, it was assumed that the coagulation dynamics is in the free-molecular regime. A size-independent enhancement factor of 2.2, based on the results of Harris and Kennedy,<sup>24</sup> was used in calculations of collision frequencies.

Beginning with the dimers, the forming clusters were assumed to be "solid phase" and allowed to add and lose mass by surface reactions



where  $C_{\text{soot-H}}$  represents an arm-chair site on the soot particle surface and  $C_{\text{soot}}^{\bullet}$  the corresponding radical. This mechanism is adopted based on the postulate<sup>25-27</sup> that the H-abstraction/ $C_2H_2$ -addition (HACA) reaction sequence<sup>3</sup> is responsible for high-temperature growth of all forms of carbonaceous materials. Wieschnowsky *et al.*<sup>28</sup> also suggested that the HACA reactions<sup>3,6</sup> "offer a key to the understanding of a number of phenomena" observed in their flame study.

Estimation of the rate coefficients of the heterogeneous reactions was based on analogous gas-phase reactions of one-ring aromatics, benzene and phenyl. The reference gaseous reactions for heterogeneous reactions (2)–(5) were the corresponding gas-phase reactions in Table (2). Oxidation by OH, reaction (6), was assumed to proceed with the collision efficiency of 0.13, based on the results of Neoh *et al.*<sup>29</sup> The particle dynamics — the evolution of soot particles undergoing simultaneous nucleation, coagulation and surface reactions described above — was modeled by a method of moments (Method II of Ref. 30). This method does not require the assumption of a particle size distribution function (PSDF). The closure of the differential equations for the PSDF moments is accomplished by interpolation between the moments.<sup>22,30</sup> The numerical integration of the moment equations took from 20 to 50 s on an IBM 3090/600S main-frame computer.

Figures 7 and 8 present the results computed using the model discussed above for two of the chosen flames: Flame B — flame No. 1 of Bockhorn and co-workers<sup>28</sup> — 25.4%  $C_2H_2$  – 19.6%  $O_2$  – Argon, pressure 90 torr; and Flame H — an atmospheric 16.5%  $C_2H_4$  – 17.9%  $O_2$  – Argon, of Harris and co-workers.<sup>31</sup> Both flames were computed with the same kinetic model, assuming  $A_4$  (pyrene or acepyrene) to be the  $A_I$  species which initiates the planar growth of PAHs and the formation of particles, parts (II) and (III) of our model, respectively. Changing  $A_I$  affects strongly the rate of particle nucleation.

It can be seen in Figs. 7 and 8 that the model predictions are in relatively close agreement with experiment for the initial, particle inception part of the flames; however, the computed and experimental results begin to deviate from one another with increasing flame height. One factor identified as a cause of this disagreement is the shape of the PAH profiles. This is demonstrated in Fig. 7, where it is shown that using a narrower (experimental-like<sup>8</sup>) profile for  $A_4$  improves the agreement between the model and experiment for Flame B. It was also computed that PAH condensation on the particle surface is sufficiently fast to significantly affect the PAH profiles in the post-flame zone.

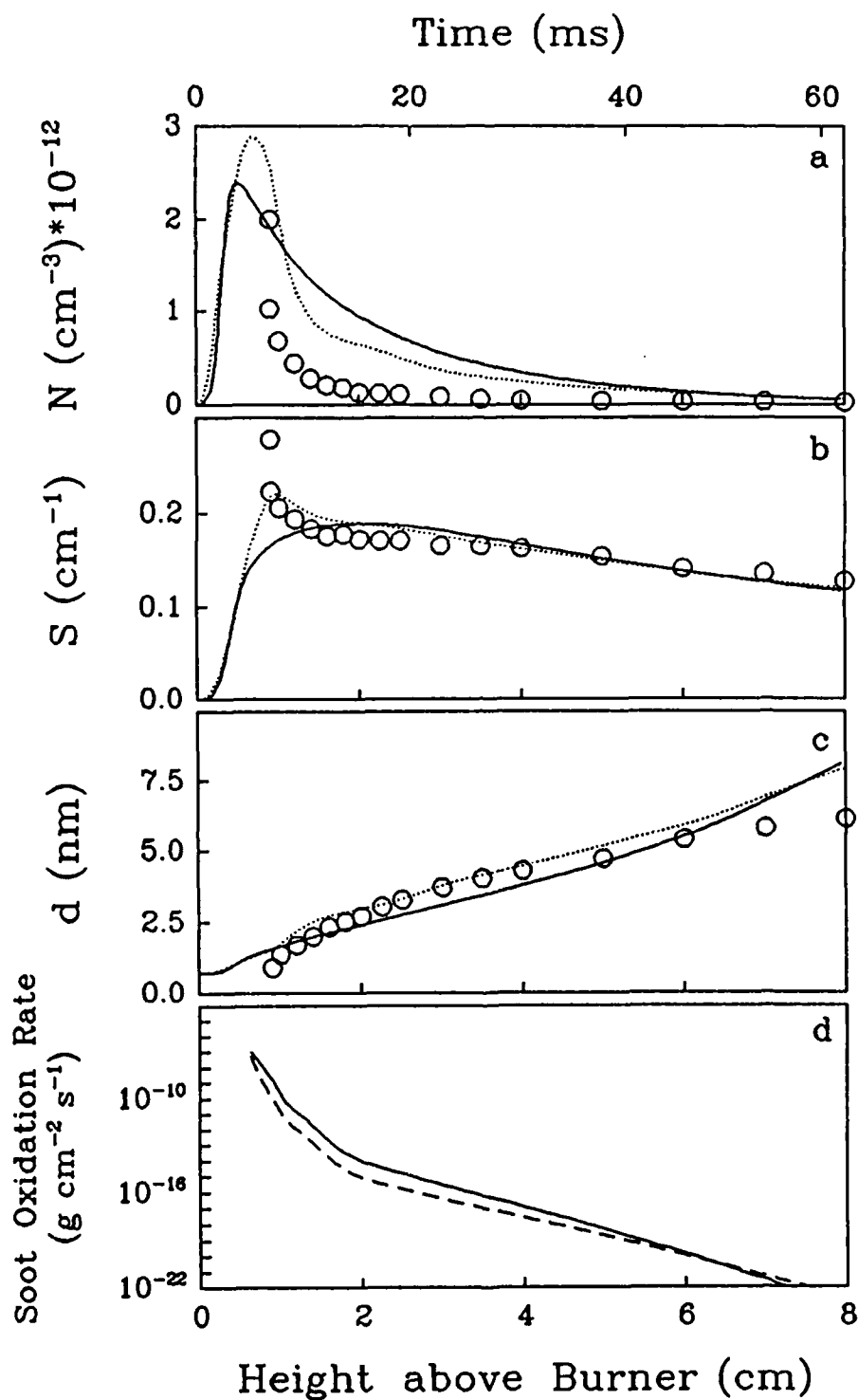


Fig. 7. Comparison of model predictions and experimental data for Flame B: (a) particle number density; (b) particle surface area; (c) average particle diameter [circles – experimental results,<sup>28</sup> solid lines – model prediction, dotted lines – model prediction using an experimental-like profile for A<sub>4</sub>]; (d) specific rate of soot particle oxidation by O<sub>2</sub> [solid line – model prediction, dashed line – from the expression of Nagle and Strickland-Constable.<sup>33</sup>

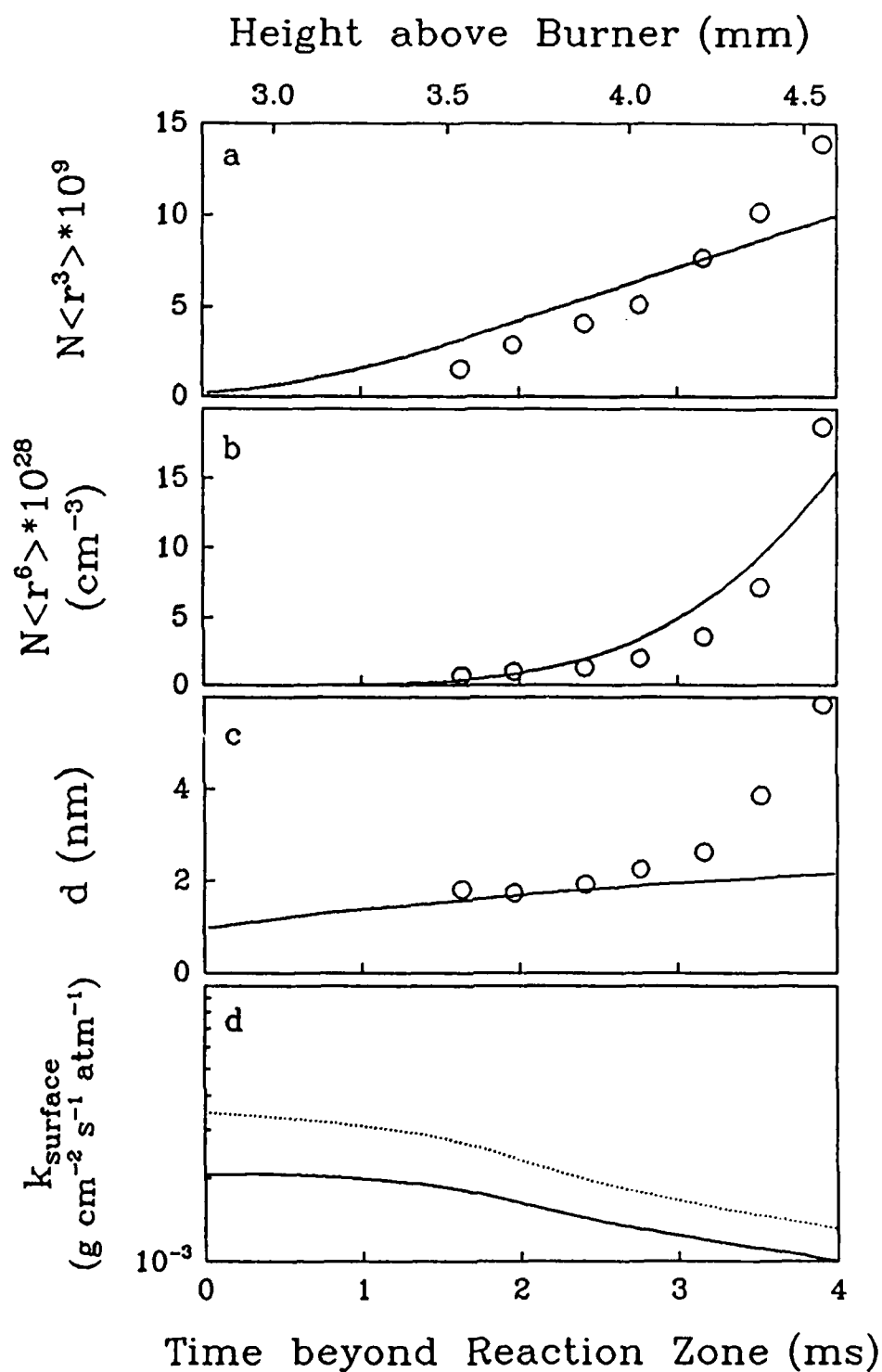


Fig. 8. Comparison of model predictions and experimental data for Flame H: (a)–(c)  $N$  – particle number density,  $r$  – particle radius,  $\langle r^p \rangle$  – average  $r^p$ ,  $d$  – average particle diameter, circles – experimental results,<sup>31</sup> solid lines – model prediction; (d) specific surface growth rate coefficient.

As expected from the dynamics of Smoluchowski coagulation, the computed rate of nucleation is balanced by the rate of coagulation throughout the particle inception zone. Particle inception is primarily determined by PAH coagulation, initiated and controlled by PAH coalescence into dimers. Our model describes the surface processes in terms of elementary reactions of active sites. The density of active sites is determined by the gas-phase environment — by the competition among reactions (2) – (6). Hence, the dissimilarity in surface growth behavior can be explained by the difference in the dynamics of active sites. Our model resolves the controversy brought up recently by Bockhorn and co-workers,<sup>28</sup> who observed that the surface growth rate is independent of the surface area of soot particles, contrary to Harris and Weiner,<sup>32</sup> who postulated that the rate of surface growth is first order in particle surface area. Also, the computed net surface growth rate is computed to be in close agreement with that determined by Harris and Weiner<sup>32</sup> (Fig. 8d) and the predicted rate of soot oxidation by O<sub>2</sub> agrees well with the expression of Nagle and Strickland-Constable<sup>34</sup> (Fig. 7d).

Our model predicts what is essentially the classical picture of soot particle inception:<sup>34</sup> formation of PAHs, their coagulation into clusters and cluster coagulation, and surface growth due to chemical and physical processes. The model also predicts the classical structure of soot particles:<sup>35</sup> a less dense particle core, composed of randomly oriented PAH oligomers, and a more dense concentrically-arranged particle shell.

## FUTURE WORK

The objectives for the next year are the following:

1. To complete the revision and testing of the neutral reaction mechanism of PAH production, and to prepare a manuscript reporting these results.
2. To apply the developed mechanism and computer code for soot particle nucleation and growth to other combustion environments of interest.
3. To review the ionic reaction mechanisms, which will be supply to us by AeroChem.
4. To perform flame simulations with the ionic mechanism(s) of (3) above.
5. To analyze the computational results of (4) above.

## PRESENTATIONS AND PUBLICATIONS

1. Frenklach, M., "Particulate Formation in Hydrocarbon Combustion." Invited seminar at the University of Cincinnati, Department of Chemical and Nuclear Engineering, February 2, 1989.
2. Frenklach, M., "Formation of PCA," Prepared statement at the workshop on "Current Problems in Soot Formation during Combustion, Especially the Mechanism of Soot Formation," the Commission on Condensation, Academy of Sciences Göttingen, FRG, March 29-30, 1989.
3. Frenklach, M., "Surface Growth," Prepared comment at the workshop on "Current Problems in Soot Formation during Combustion, Especially the Mechanism of Soot Formation," the Commission on Condensation, Academy of Sciences Göttingen, FRG, March 29-30, 1989.
4. Wang, H. and Frenklach, M., "Modeling of PAH Profiles in Premixed Flames". Paper presented at the Fall Technical Meeting of the Eastern States Section of the Combustion Institute, Albany, New York, October 1989, Paper 12.
5. Frenklach, M. and Wang, H., "Detailed Modeling of Soot Particle Nucleation and Growth." Paper submitted to the Twenty-Third International Symposium on Combustion.
6. Frenklach, M., "Reduction of Chemical Reaction Models." In *Numerical Approaches to Combustion Modeling* (E. S. Oran and J. P. Boris, Eds.), Am. Inst. Aeronautics Astronautics Prog. Ser., in press.

## PROFESSIONAL PERSONNEL

Dr. Michael Frenklach — Principal investigator

Mr. Hai Wang — Graduate student

## INVENTIONS

None.

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